

Langmuirian Blocking of Irreversible Colloid Retention: Analytical Solution, Moments, and Setback Distance

Feike J. Leij,* Scott A. Bradford, Yusong Wang, and Antonella Sciortino

Abstract

Soil and aquifer materials have a finite capacity for colloid retention. Blocking of the limited number of available retention sites further decreases the rate of retention with time and enhances risks (e.g., pathogens or colloid-associated contaminants) or benefits (e.g., remediation by microorganisms or nanoparticles) of colloid migration. Our objective was to use a straightforward procedure, based on variable transformation and Laplace transform, to solve the problem of advective colloid transport with irreversible retention and Langmuirian blocking for a pulse-type condition. Formulas for the mean breakthrough time and retardation factor were obtained using zero- and first-order time moments of the breakthrough curves. Equations for the time and position (setback distance) for a particular colloid concentration were obtained from this information. *Escherichia coli* D21 g breakthrough curves and retention profiles in fine sand at four ionic strengths were well described by the model when parameters were optimized. Illustrative simulations demonstrated that blocking becomes more important for smaller retention capacity (S_m) and for larger retention rate coefficient (k), input concentration (C_o), and pulse duration. Blocking tended to delay colloid arrival time at a particular location relative to a conservative tracer, and produced larger setback distances for smaller k and S_m/C_o .

Core Ideas

- Analytical solution for blocking of colloid retention.
- Determination of zero and first moments.
- Expressions for setback distance and arrival time.
- Simulation of *Escherichia coli* D21g transport and retention.

KNOWLEDGE OF the transport and fate of natural colloids such as microbes, clay minerals, rock fragments, and organic debris as well as engineered nanoparticles is important. For example, colloids may facilitate the movement of low-solubility contaminants (Grolmund et al., 1996; Šimůnek et al., 2006), pathogenic microbes directly pose a threat to human health (Gerba et al., 1996; Abbaszadegan et al., 2003), and colloids may affect the hydraulic properties of the subsurface (Yuan and Shapiro, 2012). Transport of colloids is often described using the advection–dispersion equation with kinetic terms for retention and release between the aqueous and solid phases (Bradford et al., 2002; Bedrikovetsky et al., 2011; Wang et al., 2013; Neukum et al., 2014). Colloid release is frequently negligible under steady physicochemical conditions, and colloid retention can be modeled as an irreversible process (Johnson et al., 1996; Ryan and Elimelech, 1996; Tufenkji, 2007).

Most colloid transport studies have considered clean bed conditions by assuming a constant rate of retention (k) and a corresponding infinite retention capacity (e.g., Ryan and Elimelech, 1996). In reality, soil and aquifer material will always have a finite retention capacity, and only a small fraction of the solid surface area may contribute to colloid retention even under so-called favorable attachment conditions (Treumann et al., 2014; Sasidharan et al., 2014). The maximum solid-phase colloid concentration (S_m) occurs when all available retention sites are filled. Blocking of available retention sites decreases the retention rate with time and enhances the transport of colloids.

Values of k and S_m depend on physicochemical conditions such as water velocity, solution chemistry, the colloid size and shape, pore structure and microscopic surface roughness, and nanoscale physical and chemical heterogeneity (Bradford et al., 2013). The sensitivity of k and S_m to physicochemical conditions produces a diversity of retention and blocking behaviors. Blocking can produce breakthrough curves that are asymmetric or delayed depending on the values of k and S_m , the input concentration, and the pulse duration (Torkzaban et al., 2012; Liang et al., 2013a, 2013b; Sasidharan et al., 2014). The shape of the profile of retained colloids has been reported to transition as a result of blocking (Liang et al., 2013a). Because blocking

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produces increased risks of colloid migration, it is important to elucidate and quantify the physicochemical conditions that affect blocking.

A number of models have been developed to describe blocking behavior. The Langmuirian dynamics model assumes that k decreases in a linear fashion with increasing amounts of retention (Adamczyk et al., 1994), whereas the random sequential adsorption model considers a nonlinear decrease in k with the amount of retention (Johnson and Elimelech, 1995). The blocking function for colloids can be based on that for “hard spheres” with modifications for electrostatic double-layer and hydrodynamic interactions (Ko et al., 2000). The difference between the Langmuirian and the random sequential adsorption model is small for low coverage (Camesano et al., 1999), and the simpler second-order kinetic Langmuir model is still quite popular (e.g., Deshpande and Shonnard, 1999; Neukum et al., 2014). Langmuirian blocking will be used in this study to facilitate analytical solution of the transport problem. Although numerical methods are commonly used to quantify colloid transport (e.g., Šimůnek et al., 2008), analytical methods provide some advantages over numerical approximations. Analytical solutions can be useful to verify numerical solutions, to elucidate the role of model parameters and inversely determine the value of unknown parameters, and to quickly and easily simulate transport behavior at larger temporal and/or spatial scales (Javandel et al., 1984; Vanderborght et al., 2005). Furthermore, moments can be derived from analytical solutions to provide information on the properties of the breakthrough curves and retention profiles. For example, such information could be used in risk assessment to determine the mean breakthrough time and the setback distance where a colloid concentration occurs at a specific time.

The problem of colloid transport in porous media with nonlinear kinetics and Langmuirian blocking is similar to that of the more widely studied case of transport during ion exchange. This problem was first solved by Bohart and Adams (1920), who studied the absorption of Cl^- in air by a charcoal bed. In this case, the rate of sorption depends on the Cl^- concentration as well as the residual sorption capacity of the charcoal. They solved the problem for a step-type input by manipulating two first-order rate equations using elementary properties of partial differentiation. Related problems have been widely studied in physical chemistry and chemical and environmental engineering, with some recent applications, among others, by Vijayaraghavan and Yun (2008) and Han et al. (2009). Other mathematical solutions have been based on characteristic lines (e.g., Golshan-Shirazi and Guiochon, 1989; Gritti and Guiochon, 2013) or traveling waves (Van Duijn and Knabner, 1992a, 1992b).

The objective of this study is to use a straightforward procedure, based on variable transformation and Laplace transform, to solve the problem of colloid transport with irreversible retention and Langmuirian blocking for a pulse-type condition. The mathematical model includes advective colloid transport but, consistent with results from many packed laboratory column studies, neglects hydrodynamic dispersion. The analytical solution is used to optimize parameter values to *E. coli* D21g concentrations from column displacement experiments. The solution is further used to derive the mean breakthrough time and retardation factor based on expressions for the zero- and first-order moments and the setback distance and travel time for a particular efflu-

ent colloid concentration. Simulated breakthrough curves and retention profiles are presented to illustrate the sensitivity of transport and blocking to model parameters.

Mathematical Problem

Analytical Solution

The problem involves colloid transport during one-dimensional steady water flow with negligible hydrodynamic dispersion in a porous medium that is completely saturated with water. An influent solution with a uniform colloid concentration is supplied for a finite time to an initially colloid-free porous medium. There is colloid partitioning between the aqueous and solid phases according to a Langmuirian model. The mathematical problem may be written as

$$\frac{\partial C}{\partial t} + \frac{\rho}{\theta} \frac{\partial S}{\partial t} + V \frac{\partial C}{\partial z} = 0 \quad [1]$$

$$\frac{\rho}{\theta} \frac{\partial S}{\partial t} = \psi k C \quad [2]$$

subject to

$$C(0, t) = C_o H(t_o - t) \quad [3a]$$

$$C(z, 0) = 0 \quad [3b]$$

where θ is the volumetric water content, C and S are the aqueous and solid-phase concentrations expressed as either the number of particles or colloid mass per aqueous volume and solid mass, respectively, C_o is the colloid concentration of the inlet solution, H is the Heaviside or unit-step function, t is time, t_o is the time that colloid is applied at the column inlet (pulse duration), z is distance from the column inlet, V is the pore-water velocity, ψ is a dimensionless function to account for site “blocking,” k is the “clean-bed” first-order retention coefficient, and ρ is the bulk density. Blocking of colloid retention is modeled using the following Langmuirian type of equation (Adamczyk et al., 1994; Wang et al., 2013):

$$\psi = \frac{S_m - S}{S_m} \quad [4]$$

where S_m is the maximum solid-phase concentration of colloids. Equation [2] produces a second-order expression for irreversible retention and Langmuirian blocking. The rate equation turns into the more familiar first-order expression when S_m is much larger than S , for example for small k .

The appendix details the solution procedure for a pulse-type inlet condition, which may also be followed for other influent conditions. The solutions for the aqueous and solid concentrations are given by

$$C(z, t) = \frac{C_o}{G(z, t)} \left\{ H[z - V(t - t_o)] - H(z - Vt) \right\} \times \exp \left[\frac{k C_o}{Q_E V} (Vt - z) \right] \quad [5]$$

$$S(z, t) = S_m - \frac{S_m}{G(z, t)} \exp \left(\frac{kz}{V} \right) \quad [6]$$

with

$$G(z, t) = \exp\left(\frac{kz}{V}\right) - H(Vt - z) + \left\{ H[z - V(t - t_o)] - H(z - Vt) \right\} \times \exp\left[\frac{kC_o}{Q_m V}(Vt - z)\right] + H[V(t - t_o) - z] \exp\left[\frac{kC_o t_o}{Q_m}\right] \quad [7]$$

where Q_m is the maximum solid concentration expressed per volume of aqueous phase using

$$Q_m = \frac{\rho S_m}{\theta} \quad [8]$$

Zero- and First-Order Moments

Time moments of the effluent concentration are defined as

$$m_n(z) = \int_0^\infty \frac{t^n C(z, t)}{C_o} dt \quad [9]$$

where $m_n(z)$ is the n th order time moment at location z . The zero (m_0) and first (m_1) order moments are obtained by substituting Eq. [5] into Eq. [9] and subsequent integration. The expressions for m_0 and m_1 are

$$m_0 = t_o + \frac{1}{b} \ln \left\{ \frac{a + \exp[-b(t_o + z/V)]}{a + \exp(-bz/V)} \right\} \quad [10]$$

$$m_1 = t_o \left(\frac{t_o}{2} + \frac{z}{V} \right) - \frac{Q_m}{C_o} \frac{z^2}{V^2} - \frac{1}{b^2} \left\{ \text{Li}_2 \left[-\frac{\exp[-b(t_o + z/V)]}{a} \right] - \text{Li}_2 \left[-\frac{\exp(-bz/V)}{a} \right] \right\} + \frac{t_o + z/V}{b} \ln \left\{ \frac{\exp[-b(t_o + z/V)]}{a} + 1 \right\} \quad [11]$$

with auxiliary variables a and b defined as

$$a = \frac{\exp(-bz/V)}{\exp(kz/V) - 1} \quad [12a]$$

$$b = \frac{kC_o}{V} \quad [12b]$$

The dilogarithmic function Li_2 is evaluated for arguments with an absolute value of less than unity according to series expansion 27.7.2 of Abramowitz and Stegun (1972) or by numerical integration using Gauss-Chebyshev quadrature.

Colloid particles that are not retained will have the same residence time in the soil. The mean of the colloid breakthrough curve will lag behind that of water due to nonlinear retention.

Colloids that are applied early on have a greater likelihood of becoming retained than those applied when the number of available retention sites has diminished. The delay due to retention can be quantified with the mean breakthrough time (M_1) and the retardation factor (R):

$$M_1 = \frac{m_1}{m_0} \quad [13a]$$

$$R = \frac{M_1}{z/V + t_o/2} \quad [13b]$$

It should be noted that unlike the conventional use of the retardation factor to quantify the delay of all applied solute due to (reversible) reactions with the solid phase (cf. Fitts, 2002; Leij and Sciortino, 2012), Eq. [13] applies only to colloids that are not (irreversibly) retained.

Setback Distance and Travel Time

It may be desirable to quantify where or when a particular critical concentration is reached at a specified time or location, respectively. Expressions for the setback distance $z(C, t)$ and the travel time $t(C, z)$ are presented below for a step-type colloid input to make such estimates.

Direct inversion of Eq. [5] is not feasible to determine a closed-form expression for $z(C, t)$, and simplifying assumptions will have to be made. Of particular interest is the distance at which small amounts of colloid start to appear in the subsurface after a given time. This occurs at relatively large distances z , when the following approximate expression may be obtained:

$$z(C, t) = \frac{VQ_m}{k(C_o + Q_m)} \left[\frac{kC_o t}{Q_m} + \ln \left(\frac{C_o}{C} - 1 \right) \right] \exp(kz/V) \gg 1, \quad 0 < z < Vt \quad [14]$$

A retardation factor R_z may be defined as the ratio of the distance advanced by water and the colloid setback:

$$R_z(C, t) = \frac{C_o + Q_m}{C_o + (Q_m/kt) \ln(C_o/C - 1)} \quad [15]$$

To determine the travel time before a specific concentration is reached, the solution for a step input according to Eq. [5] is inverted and rearranged to obtain

$$t(C, z) = \left(\frac{Q_m}{kC_o} \right) \left[\ln \left(\frac{C}{C_o - C} \right) + \frac{zk(1 + C_o/Q_m)}{V} \right] \quad [16]$$

$t > z/V$

A retardation factor R_t can now be defined as the ratio of travel time for the colloid to the travel time for water (i.e., z/V):

$$R_t(C, z) = 1 + \frac{Q_m V}{kC_o z} \ln \left[1 - \exp \left(\frac{kz}{V} \right) \right] \quad [17]$$

Description of Experimental Data

The analytical solution for negligible dispersion was used to describe effluent curves and retention profiles of *E. coli* D21g obtained by Wang et al. (2013). The effective diameter of *E. coli* D21g is 1.84 μm , which will potentially reduce retention because S_m is inversely related to the square of the colloid size (Bradford et al., 2013). A 30-min pulse of *E. coli* D21g was applied to an initially microbial-free sand column during steady water flow with ionic strengths of 1, 5, 20, and 100 mmol L^{-1} . Figure 1a shows the observed effluent concentrations, and Fig. 1b contains the retention profiles obtained by destructive sampling at the end of the displacement experiment. Higher ionic strengths will diminish repulsive forces between microbes and the solid phase, which results in enhanced retention of *E. coli* D21g by the porous medium and lower effluent concentrations. Equations [5] and [6] were used to describe the data by optimizing the parameters V and k using the Gauss–Marquardt procedure (Marquardt, 1963). Table 1 contains experimental information reported by Wang et al. (2013) and optimized values for V and k as well as the coefficient of determination and root-mean square error:

$$\text{RMSE} = \sqrt{\frac{1}{(N-p)C_o^2} \left[\sum_{i=1}^{N_a} (C_i - \hat{C}_i)^2 + \sum_{i=1}^{N_s} (S_i - \hat{S}_i)^2 \right]} \quad [18]$$

where N_a and N_s are the number of effluent and in situ samples ($N = N_a + N_s$), p is the number of optimized parameters, and the caret denotes an optimized variable. Figure 1 includes optimized curves as well. A reasonably good description of the observations could be obtained, although the analytical model did not provide as good of a description as the numerical solution (Wang et al., 2013) because it does not include dispersion. There is very little retention for ionic strength (IS) = 1 mmol L^{-1} , and the gradual increase of concentration in the breakthrough curve can obviously not be reproduced in the absence of dispersion. Optimized values for k and reported values for S_m increase with IS. The optimization is most accurate for IS = 100 mmol L^{-1} when the lack of colloid in the effluent obviates the need for a model with dispersion.

Predictions with Analytical Results

Results for step displacement ($t_o \rightarrow \infty$) to illustrate the effect of the retention rate k are provided in the supplemental material. Supplemental Fig. S1 provides illustrative examples of normalized solid and aqueous concentrations as a function of depth for several values of k (10, 1, and 0.1 min^{-1}) in the presence and absence of Langmuirian blocking. Additional examples of solid and aqueous concentrations and the partitioning of colloid

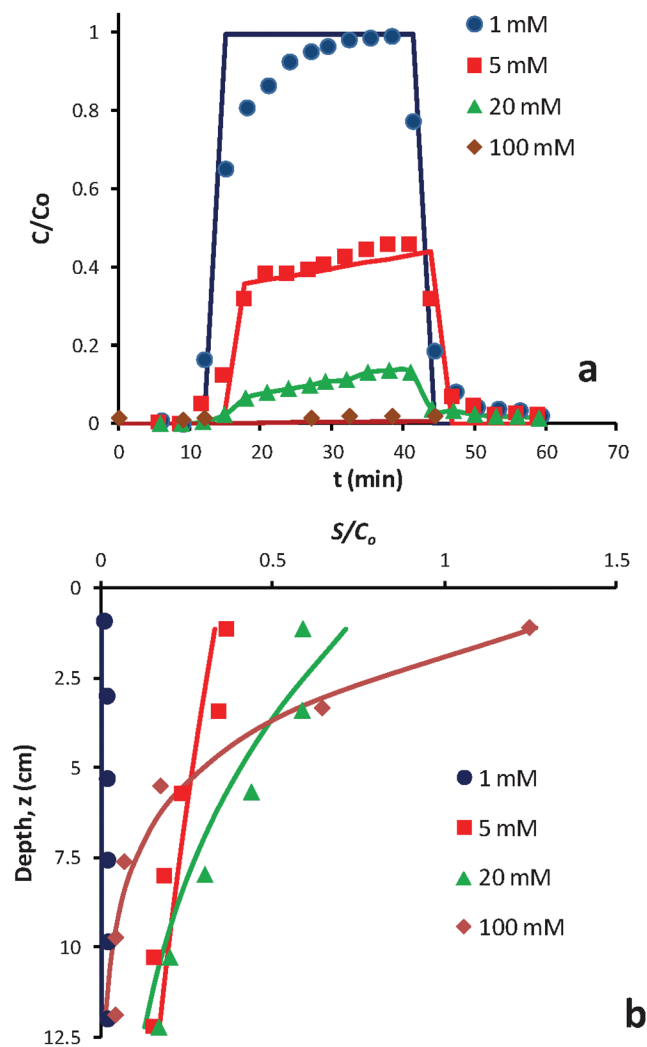


Fig. 1. Normalized observed and modeled *Escherichia coli* D21g concentrations as a function of (a) time and (b) depth for four different ionic strengths.

between solid and aqueous phases are provided in Supplemental Fig. S2 and S3, respectively, when blocking is considered. In the following, results are shown for the newly derived solutions for a pulse input.

Figure 2 shows breakthrough curves and retention profiles for the application of a 60-min colloid pulse, with parameter values that correspond to those reported by Wang et al. (2013), to illustrate how k , S_m , and C_o contribute to blocking. Retention rates are varied for Fig. 2a and 2b. Little colloid is retained for $k = 0.01 \text{ min}^{-1}$, and the colloid front shows up in the effluent with a high concentration that increases very slowly with time until colloid application is stopped. Conversely, solid concentrations are relatively small. For the intermediate $k = 0.1 \text{ min}^{-1}$, the colloid

Table 1. Experimental and optimized parameters for *Escherichia coli* D21g displacement, including the position for effluent curves from the column inlet (L), time of sampling for in situ profiles (t), optimized pore water velocity (V), optimized attachment coefficient (k), and the ratio of the maximum solid-phase concentration (S_m) to the (aqueous) influent concentration (C_o , $\approx 10^8 \text{ cm}^{-3}$) for four different ionic strengths (IS).

IS	L	t	V	k	S_m/C_o	r^2	RMSE
mmol L^{-1}	cm	min	cm min^{-1}	min^{-1}	$\text{cm}^3 \text{g}^{-1}$		
1	13.3	59.3	0.925	0.0004	0.01	0.932	0.1143
5	13.3	58.8	0.820	0.0643	1.1	0.921	0.0488
20	13.0	59.1	0.871	0.150	3.5	0.932	0.0453
100	13.3	44.5	0.751	0.325	4.8	0.992	0.0341

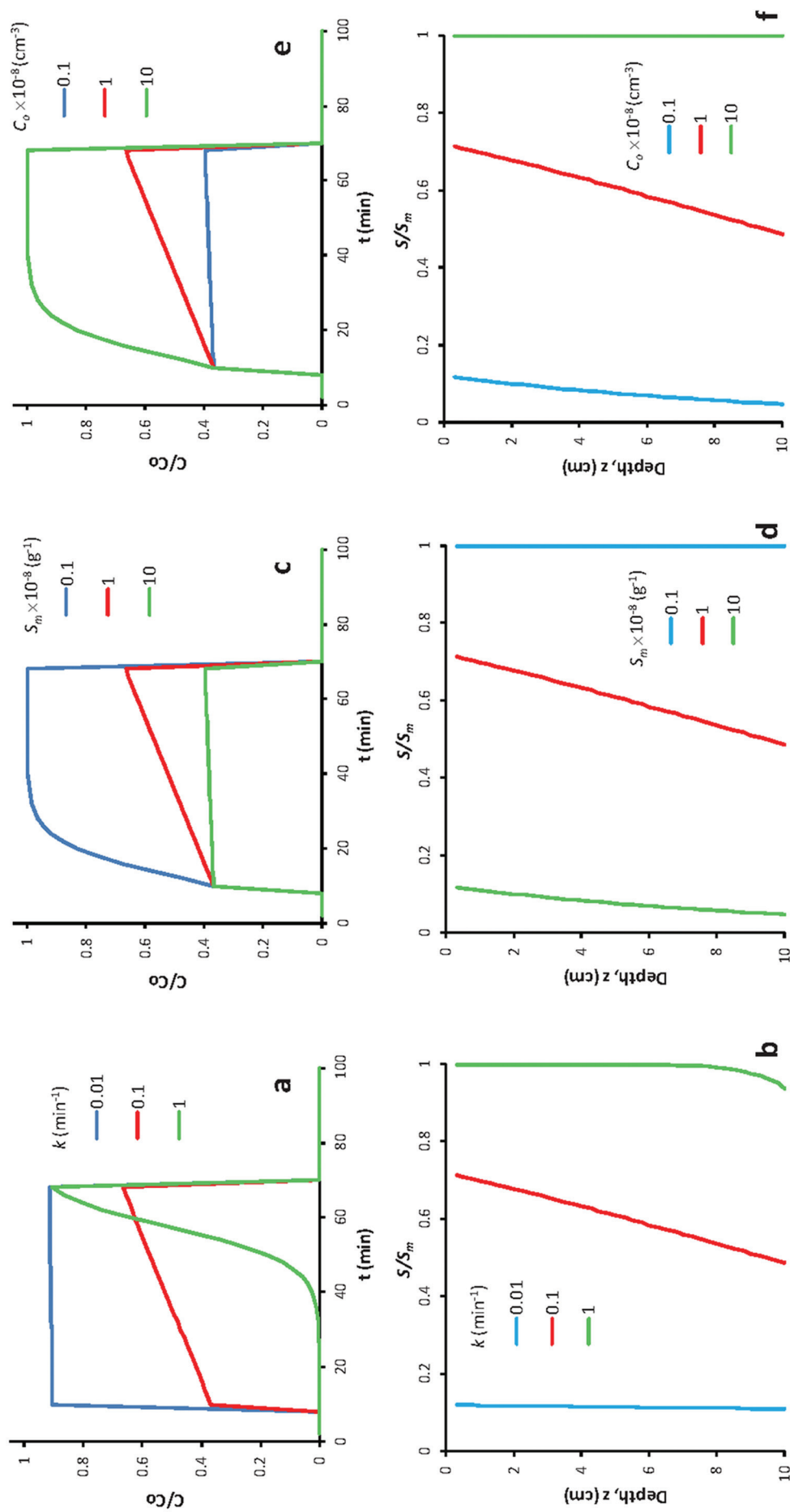


Fig. 2. Breakthrough curves (a,c,e) at depth $z = 10 \text{ cm}$ and retention profiles (b,d,f) at time $t = 100 \text{ min}$ for optimized pore water velocity $V = 1 \text{ cm min}^{-1}$, bulk density $\rho = 1.7 \text{ g cm}^{-3}$, volumetric water content $\theta = 0.36$, and pulse duration $t_p = 60 \text{ min}$: (a,b) three different retention rates k , with influent concentration $C_0 = 10^8 \text{ cm}^{-3}$ and maximum solids concentration $S_m = 10^8 \text{ g}^{-1}$; (c,d) three different S_m values, with $k = 0.01 \text{ min}^{-1}$ and $C_0 = 10^8 \text{ cm}^{-3}$, and (e,f) three different C_0 values, with $k = 0.01 \text{ min}^{-1}$ and $S_m = 10^8 \text{ g}^{-1}$.

first appears in the effluent at about the same time as for $k = 0.01$ min^{-1} but at a far smaller value. Subsequently, the concentration increases more rapidly (Fig. 2a). For the high retention ($k = 1$ min^{-1}), breakthrough is considerably later with a gradual increase in C/C_o once it occurs; retention is still not instantaneous for this rate. Notice that after 68 min, $C/C_o = 0.665$ for $k = 0.1$ min^{-1} is lower than the corresponding value of $C/C_o = 0.907$ when $k = 1$ min^{-1} . After 60 min, the values for S/S_m have not reached yet unity for $k = 1$ min^{-1} and colloid that is blocked out appears in the effluent. The differences in initial breakthrough time and final effluent concentrations are due to blocking and the irreversibility of the retention. Breakthrough curves (Fig. 2c) and colloid profiles (Fig. 2d) were obtained for three different values of the maximum amount that can be retained. The same amount of colloid was applied in all three cases. Although colloid first appears in the effluent at the same time for all three S_m , the effluent concentration is higher for the lower $S_m = 0.1 \times 10^8$ colloids g^{-1} of medium (Fig. 2c), while the relative amount in the solid is also highest for this S_m (Fig. 2d). These findings can be explained based on mass balance considerations. The effect of the influent concentration C_o , expressed in number of colloids per volume of aqueous solution, on breakthrough curves and profiles (Fig. 2e and 2f) is just the opposite as that for S_m . The effect of application time t_o on breakthrough is shown for three different retention rates in Supplemental Fig. S4.

Retardation

Because the amount of retention sites is finite, the values for m_o and R will depend on the amount of applied colloid in absolute (i.e., t_o) and relative (i.e., Q_m/C_o) terms. Figure 3 shows the retardation factor R as a function of application period t_o (Fig. 3a) and the ratio of maximum solid to applied aqueous concentration Q_m/C_o (Fig. 3b) for three different retention rates. For small t_o , the value for R will be equal to unity regardless of the retention rate. For the higher k of 1 min^{-1} , the maximum R occurs at $t_o = 10$ min when the amount of applied colloid equals the amount of retention sites. Longer application times cause R

to decrease because no retention sites are available. In the case of lower k , much greater values for t_o are needed for the solid concentration to reach Q_m , and the values for R will be smaller and change more gradually with t_o (Fig. 3a). A similar trend can be observed when the retardation factor is plotted vs. the ratio of maximum solid to applied aqueous concentration (Fig. 3b). The amount of applied colloid ($VC_o t_o$) matches the amount of available retention sites (Q_m) when $Q_m/C_o = 1$. For $k = 1$ min^{-1} , the highest R occurs when $Q_m/C_o = 1$. The maximum R , although close to unity, is reached at a considerably lower Q_m/C_o because retention is mostly constrained by the rate constant k and less by the availability of sites. The effect of the retention rate (k) on the amount of colloid in the breakthrough curve (m_o) and its velocity relative to the pore-water velocity (R) is further illustrated in Supplemental Fig. S5.

Setback Distance and Travel Time

The approximate solution for the setback distance is illustrated to determine the distance at which smaller concentrations may occur after 60 d under field conditions. The distance is plotted as a function of normalized aqueous concentration for three retention coefficients in Fig. 4. Figure 4a shows that the colloid moves at virtually the same speed as water, which has a "setback distance" of 86.4 m due to a lack of retention sites and blocking regardless of the value for k . Low colloid concentrations occur at 86.4 m for the lowest retention coefficients ($k = 10^{-4}$ min^{-1}), while for higher coefficients, no colloid appears for distances >20 m in the case $Q_m/C_o = 10$ (Fig. 4c). Both Fig. 4b and 4c illustrate that there is a wide range of setback distances for $k = 10^{-4}$ min^{-1} , whereas for higher k , colloid concentrations have a similar setback distance. The corresponding retardation factor, R_z as computed by Eq. [15], is plotted as a function of C/C_o in Supplemental Fig. S6 for the three k values used in Fig. 4 with Q_m/C_o equal to 1 or 10.

Related to the setback distance is the time that should elapse before a specified colloid concentration reaches a given position. Figure 5 shows the time for a particular concentration to reach

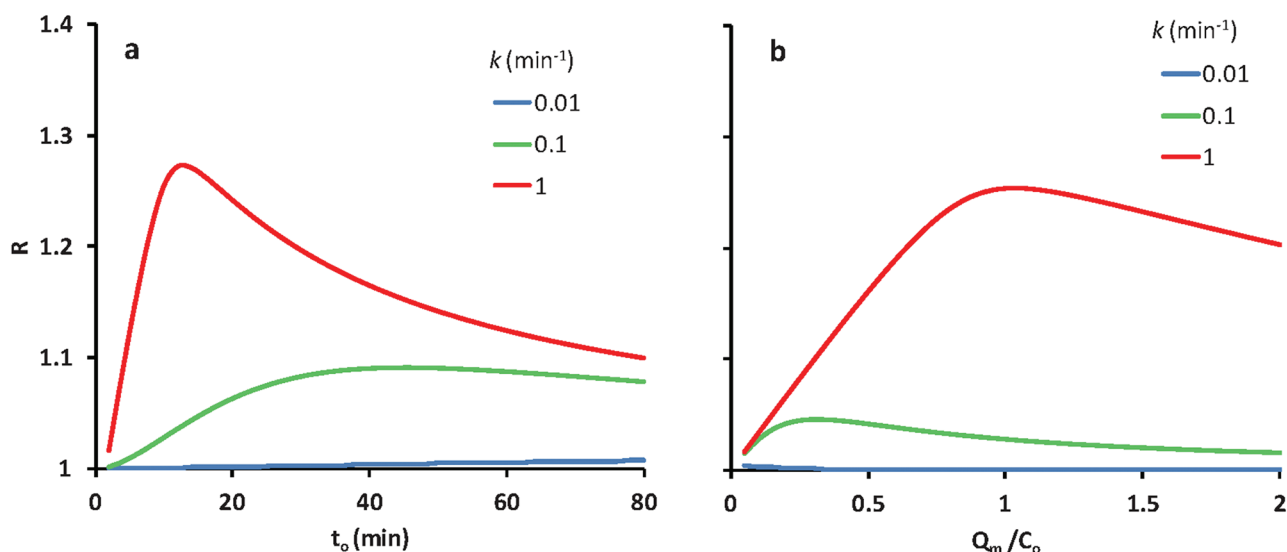


Fig. 3. Retardation factor R , according to Eq. [13b], for three retention rates k for effluent curves at $z = 10$ cm resulting from a pulse application with optimized pore water velocity $V = 1$ cm min^{-1} as a function of: (a) pulse duration t_o with influent concentration $C_o =$ volumetric maximum solids concentration Q_m and (b) the ratio of maximum solid to influent concentration Q_m/C_o with $t_o = 10$ min.

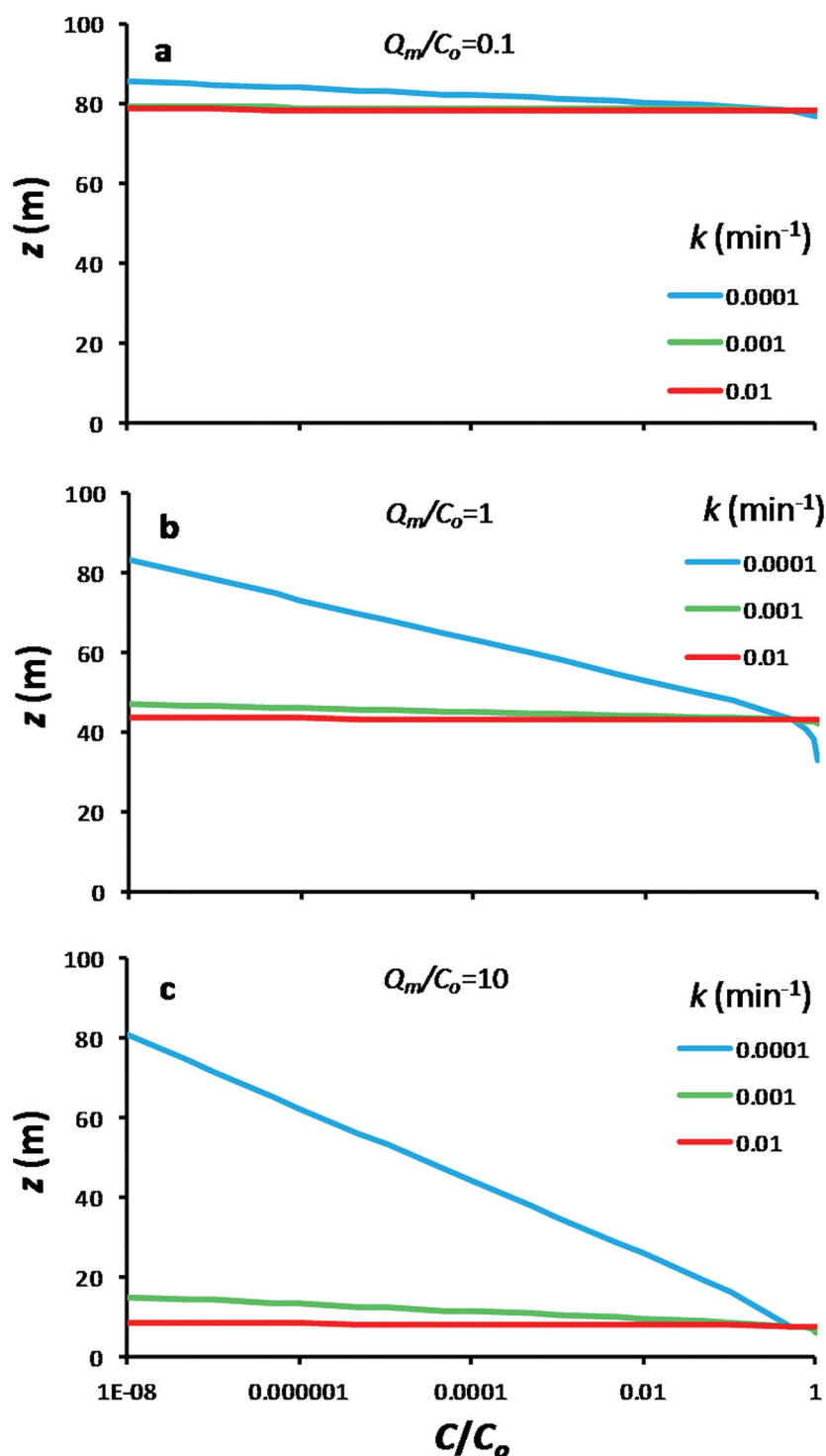


Fig. 4. Setback distance z as a function of normalized aqueous concentration C/C_o for three different retention rates after 60 d for a step application with optimized pore water velocity $V = 0.1 \text{ cm min}^{-1}$: (a) ratio of maximum solid to influent concentration $Q_m/C_o = 0.1$, (b) $Q_m/C_o = 1$, and (c) $Q_m/C_o = 10$.

a distance of 10 cm, such as at the outlet of a laboratory column. Again, for a limited amount of accessible retention sites, the colloids move at a similar speed as water (Fig. 5a). If $Q_m/C_o = 10$ (Fig. 5c), concentrations for the low retention coefficient of $k = 0.01 \text{ min}^{-1}$ travel at the same rate as water; only high concentrations C/C_o require $>10 \text{ min}$ to be achieved because the colloid front is relatively steep. For the high $k = 1 \text{ min}^{-1}$, the front is also steep and it will take $>40 \text{ min}$ for a concentration as small as $C/C_o = 0.001$ to reach the column outlet. For the intermediate $k = 0.1 \text{ min}^{-1}$, a minute amount of colloid will reach the column outlet along with water, but the higher concentrations will not be encountered until much later due to blocking.

Supplemental Fig. S7 shows the retardation factors R , defined by Eq. [17] as the ratio of travel time for a particular colloid concentration to water for the same scenario as used for Fig. 5.

Summary and Conclusions

An analytical solution for colloid transport subject to irreversible retention with Langmuirian blocking was obtained for a pulse-type input using variable transformation and Laplace transform. The developed analytical model provided a reasonable description of *E. coli* D21g breakthrough and retention profile data in fine sand at four ionic strengths. The solution was used to derive the mean breakthrough time and retardation

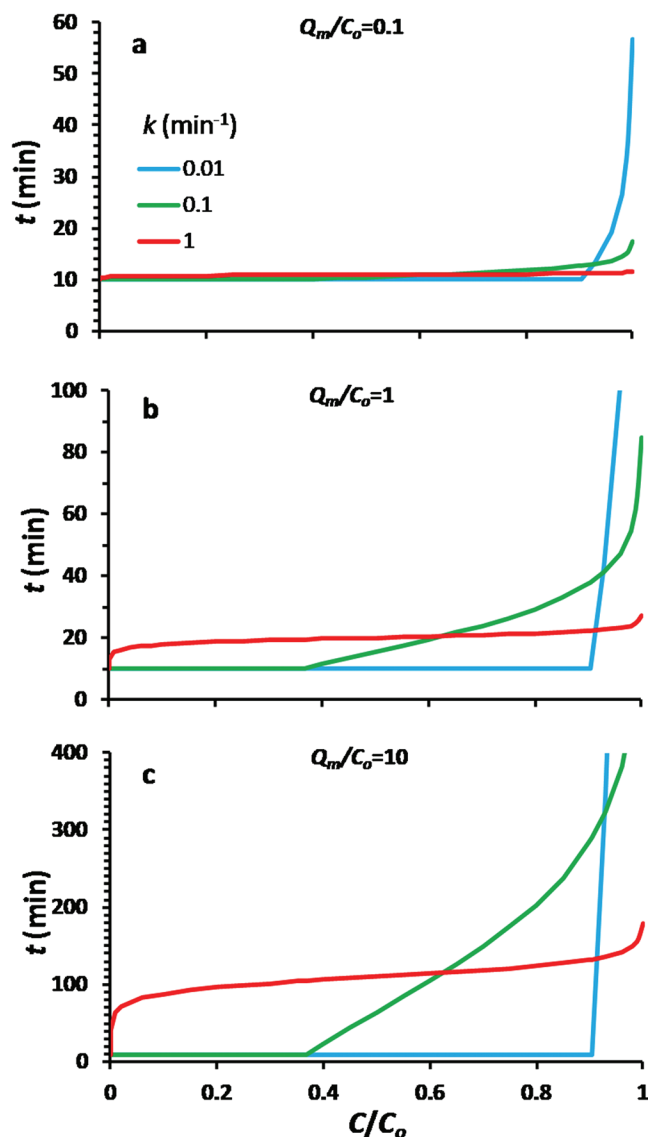


Fig. 5. Travel time t as a function of normalized aqueous concentration C/C_o for three different retention rates at depth $z = 10$ cm for a step application with optimized pore water velocity $V = 1 \text{ cm min}^{-1}$: (a) ratio of maximum solid to influent concentration $Q_m/C_o = 0.1$, (b) $Q_m/C_o = 1$, and (c) $Q_m/C_o = 10$.

factor, using expressions for zero- and first-order moments, and the setback distance and arrival time for a particular effluent colloid concentration. Simulated breakthrough curves and retention profiles demonstrate the sensitivity of colloid transport and blocking to the retention rate coefficient (k) and capacity (S_m), and the input colloid concentration (C_o) and pulse duration (t_o). In particular, blocking becomes more important for smaller S_m , and larger values of k , C_o , and t_o . Blocking was also demonstrated to have a dramatic influence on the setback distance and arrival time of colloids. Specifically, smaller k and S_m/C_o generally produces larger setback distances. The colloid arrival time at a particular location was generally delayed relative to a conservative tracer as a result of blocking. The delay in arrival was enhanced for larger values of k and S_m and smaller C_o .

Appendix

Analytical Solution Procedure

The mathematical problem may be written (subject to Eq. [3]) as

$$\frac{\partial C}{\partial t} + \frac{\partial Q}{\partial t} + V \frac{\partial C}{\partial z} = 0 \quad [\text{A1}]$$

$$\frac{\partial Q}{\partial t} = k \frac{Q_m - Q}{Q_m} C \quad [\text{A2}]$$

where Q is defined in a similar manner to Q_m using Eq. [8], with S_m replaced by S . By using the natural logarithm of the blocking function instead of the solid concentration, Eq. [A2] can be rewritten to obtain a simpler explicit expression for the aqueous concentration:

$$C = -\frac{Q_m}{k} \frac{\partial y}{\partial t} \quad [\text{A3a}]$$

$$y = \ln \left(\frac{Q_m - Q}{Q_m} \right) \quad [\text{A3b}]$$

Note that $\exp(y)$ gives the relative amount of solid sites that is still available for retention. With the help of Eq. [A3a], Eq. [A1] can now be expressed as

$$\frac{\partial^2 y}{\partial t^2} + k \exp(y) \frac{\partial y}{\partial t} + V \frac{\partial^2 y}{\partial z \partial t} = 0 \quad [\text{A4}]$$

subject to

$$\frac{\partial y}{\partial t}(0, t) = -\frac{k C_o}{Q_m} H(t_o - t) \quad [\text{A5a}]$$

$$y(z, 0) = 0 \quad [\text{A5b}]$$

$$\frac{\partial y}{\partial t}(z, 0) = 0 \quad [\text{A5c}]$$

Integration of Eq. [A4] with respect to time yields

$$\frac{\partial y}{\partial t} + k \exp(y) + V \frac{\partial y}{\partial z} = A \quad [\text{A6}]$$

where A is an integration constant that does not depend on time. From the initial conditions, it follows that $A = k$.

A second transformation is now introduced to rewrite Eq. [A6] in linear form:

$$\frac{\partial u}{\partial t} + V \frac{\partial u}{\partial z} + ku = k \quad [\text{A7a}]$$

$$u = \exp(-y) \quad [\text{A7b}]$$

subject to

$$\frac{\partial u}{\partial t} = \frac{k C_o}{Q_m} H(t_o - t) u \Big|_{z=0} \quad [\text{A8a}]$$

$$u(z,0)=1 \quad [A8b]$$

The inlet condition leads to the following solution for the inlet concentration:

$$u_o(t)=u(0,t) \\ =H(t_o-t)\exp\left(\frac{kC_o t}{Q_m}\right)+H(t-t_o)\exp\left(\frac{kC_o t_o}{Q_m}\right) \quad [A9]$$

The following Laplace transformation is applied:

$$\bar{u}(p,s)=\int_0^\infty u(z,t)\exp(-pz)dz \quad [A10]$$

to rewrite the problem as

$$\frac{d\bar{u}}{dt}+V(p\bar{u}-u_o)+k(\bar{u}-1)=0 \quad [A11]$$

with initial condition

$$\bar{u}(p,0)=\frac{1}{p} \quad [A12]$$

where p is the Laplace variable. Solution of the above problem yields

$$\bar{u}(p,t)= \\ \frac{k}{p(k+pV)}+\frac{kC_o V \exp[-(k+pV)t]}{(k+pV)[kC_o+Q_m(k+pV)]} \\ +\frac{H(t_o-t)Q_m \exp(kC_o t/Q_m)}{kC_o+Q_m(k+pV)}+ \\ +\frac{H(t-t_o)V \exp(kC_o t/Q_m)}{k+pV} \\ -\frac{H(t-t_o)kVC_o V \exp[kC_o t_o/Q_m-(k+pV)(t-t_o)]}{(k+pV)[kC_o+Q_m(k+pV)]} \quad [A13]$$

Inversion to the regular time gives

$$u(z,t)=\exp\left(\frac{-kz}{V}\right)\left\{\exp\left(\frac{kz}{V}\right)-1\right. \\ \left.+H\left(t_o-t+\frac{z}{V}\right)\exp\left[\frac{kC_o(t-z/V)}{Q_m}\right]\right. \\ \left.+H\left(t-t_o-t-\frac{z}{V}\right)\exp\left[\frac{kC_o t_o}{Q_m}\right]\right\} \quad [A14]$$

From Eq. [A3a] and [A7b], it follows that

$$C(z,t)=-\frac{Q_m}{ku}\frac{\partial u}{\partial t} \quad [A15]$$

Substitution of Eq. [A14] into [A15] yields the solution for the aqueous concentration given by Eq. [5]. From Eq. [A3b] and [A7b], it follows that

$$Q(z,t)=Q_m\left(1-\frac{1}{u}\right) \quad [A16]$$

The solid concentration given by Eq. [6] is obtained by substituting Eq. [A14] into [A16].

Supplemental Material

The supplemental material shows additional predictions and discussion for the Langmuirian blocking model. These simulations are briefly outlined above for Supplemental Fig. S1 to S7.

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